Investigations on aerosol emissions of pyrotechnic smoke generators

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Abstract: Pyrotechnic smoke generators fall under the Directive 2013/29/EU in Europe and could potentially belong to all categories except consumer fireworks. These types are especially present in the field of "Other Pyrotechnic Articles" of the categories P1 and P2, e.g. as simulation devices for paintball or airsoft gaming. The specific users of these products are aware of the corresponding smoke liberation during use and usually wear protective equipment to minimize exposure to potentially harmful aerosols. However, such products are often misused against the labelling requirements in locations where these articles are not supposed to be used, like football stadiums and demonstrations. In contrast to the intended use, uninvolved third parties are likely exposed to these reaction products without proper protective equipment. This study aims at identifying the transient particle size range of the aerosols emitted during the functioning of such common smoke generators for simulation purposes. In total four different types of articles were investigated, with five colors per type (white, blue, green, red, orange). Results show that the majority of the particles were emitted in a range between 40 nm and 350 nm, with some variation depending on the smoke color. Particles with diameters of less than 100 nm are generally of specific concern, as they can penetrate the alveolar system of the human lungs and therefore present a specific hazard.

Introduction

Each pyrotechnic article – made available on the market (of the European Community) – must be labeled with the CE marking. For achieving this conformity assessment procedures have to be carried out. The basis for these procedures is given in the directive 2013/29/EU[1] (and by the directive 2007/23/EC[2] before the entry into force of directive 2013/29/EU[1] on 1st July 2015). Different harmonized standards are applied for all types of pyrotechnic articles (fireworks, theatrical pyrotechnic articles and other pyrotechnic articles) to verify the Essential Safety Requirements (ESR) given by Annex I of the directive. These ESR cover the safe handling, the safe and correct functioning as well the physical and chemical stability of the pyrotechnic article and aspects of disposal and also health and environmental aspects etc. The corresponding harmonized standards define the test methods and the acceptance criteria to be applied. All standards define so-called "forbidden substances" regarding the requirement of maintaining a minimum risk to health during the normal use of the corresponding pyrotechnic article. Nevertheless, the standards didn't consider the health risk generated by small particles in the nanometer range. In some circumstances such articles are respirable, and in fact respirable into the alveolar systems for particles with diameters less than 100 nm. When considering smoke generators, the probability of the occurrence of such particles in large quantities is high. Many of these smoke generators are so called "other pyrotechnic articles" and are categorized in category P1 in accordance with the directive 2013/29/EU.[1] Due to the increasing number of misuses of such smoke generators (e.g. in football stadiums) and the corresponding hazard assessments, information on the transient particle size range is a key factor.

This work presents the results of the investigation on the particle emission (absolute and relative) and the particle size distribution of P1 smoke generators (subtype: "simulation device" regarding EN 16263[3]) of different colors, used for outdoor applications.

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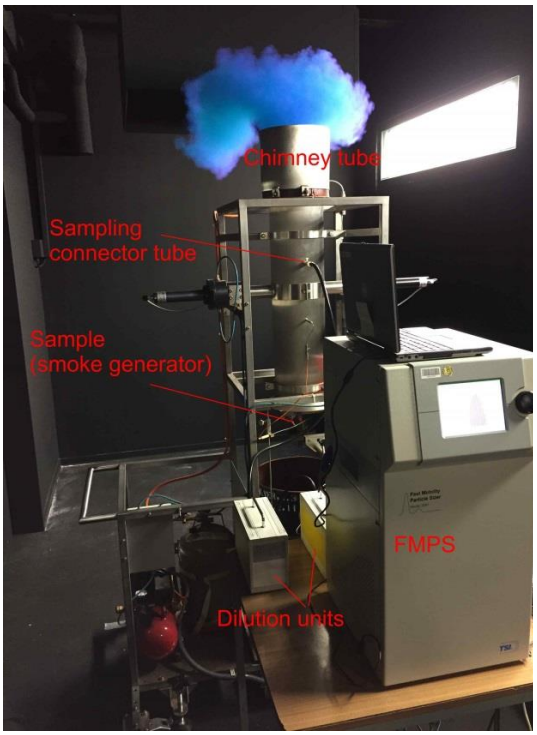

Figure 1. *Experimental setup for the FMPS measurements (front view – left)*

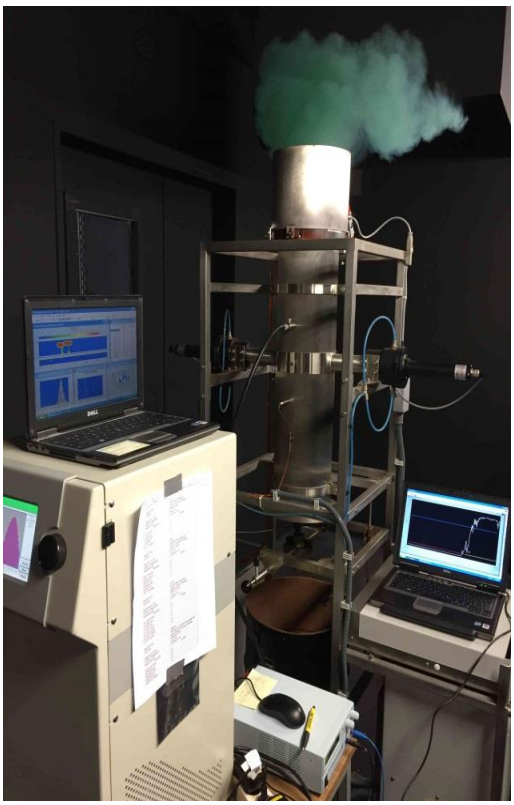

Figure 2. *Experimental setup for the FMPS measurements (front view – right)*

Experimental setup

For the following set of experiments four different types of smoke generators were tested for particle size range and concentration. For the measurement of the transient particle size distribution the device

Figure 3. *Experimental setup for the FMPS measurements (rear view)*

3091 Fast Mobility Particle Sizer (FMPS) from TSI was used.

The FMPS is a real time measurement spectrometer which offers particle size range from 5.6 to 560 nm, reporting a total of 32 channels (16 channels of size per decade). It has a flow rate of aerosol of 10 L min^{-1}. The advantages of the measurements with the FMPS are a high sensitivity, excellent wide size range, speed and working without any radioactive materials. The analysis occurs with the software FMPS 3.1.0 which has the ability to display and play back three-dimensional plots of size distribution and particle concentration against time.

The FMPS has a maximum measurement range of 108 particles per cm^3. Due to the high output of the smoke generators a dilution system was used. Two dilution units were calibrated and used upstream before the FMPS in series to get a fixed dilution rate of *ca.* 1 : 1500 which had to be considered during post-processing of the FMPS values, as well. For the measurements a custom made setup was used (Figure 1 to Figure 4). The sample was fixed over a dustbin and approximately 10 cm below a chimney tube made of steel (Ø 19 cm, length 1.2 m) with a ventilator inside. The liberated smoke was transported through the chimney tube with an average speed of *ca.* 11 m s^{-1} and vented to the outside. The smoke outside the setup device (see Figure 1) was exhausted to the outside of the building. At approximately half of the chimney tube height a connector tube was fixed for sampling of the aerosols. The emitted particles were sampled off the main stream of the ascending smoke inside

Figure 4*. Sample (smoke generator) fixing below chimney tube unit prior to ignition and functioning*

the chimney and transported into the dilution system, over a cyclone to the inlet of the FMPS for analysis. After each experimental run the dilution system had to be fully cleaned with ethanol due to the high-output smoke quantities.

Table 1 displays the main characteristics of the investigated samples (smoke generators of the subtype simulation devices).

Results

Figure 5 shows an example of the 3-D plots from the FMPS of the size distribution and particle concentration with time for a smoke generator of Type C and the color blue.

As can be seen, the smoke generation occurs over a time of about 90 s, which is in accordance with the specifications of the manufacturer for this product. The diagram illustrates that there are two particle size regions where significant emissions are identifiable. The first and the largest range can be

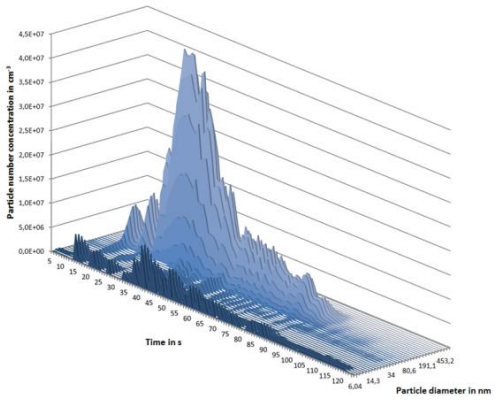

Figure 5. Transient distribution of the emitted particles of all channels of a smoke generator (Type C, color blue)

identified by particle diameters between 40 nm and 230 nm. The second range shows particle sizes between 6 nm and 12 nm (dark blue areas in Figure 5). These very small particles are of specific concern, as they can easily penetrate the alveolar lung systems of humans. Furthermore, an overall maximum regarding the emitted number of particles is observed at approximately 33 s after the ignition, with a total particle number concentration (cumulative over all channels) of $2.5.10^8$ cm^{-3}.

Figure 6 to Figure 9 illustrate the total particle number concentrations versus the particle diameters for all investigated types and the corresponding five colors white, blue, green, red, orange. For each color, two lines are displayed to check the reproducibility of the results.

As can be seen the general qualitative trend of the particle number concentrations is quite similar for all tested articles. For all four types, the colors blue and white appeared to have the highest particle number concentrations. The general reproducibility of the particle number concentrations per type and color was fair. In some cases large deviations appeared, maybe due to non-linear burning or other specific product related aspects.

The significant particle size ranges for the colors white, blue and orange were always found between *ca.* 40 nm and *ca.* 230 nm, with a maximum at

Table 1. Characteristics of the investigated samples (NEC = net explosive content)

Type	Colors	Substantials	NEC
Type A	white, blue, green, red, orange	Potassium chlorate, starch, sodium carbonate*, dyes	27–50 g
Type B	white, blue, green, red, orange	Potassium chlorate, starch, sodium carbonate*, dyes	35–60 g
Type C	white, blue, green, red, orange	Potassium chlorate, starch, sodium carbonate*, dyes	80–100 g
Type D	white, blue, green, red, orange	Potassium chlorate, starch, sodium carbonate*, dyes	40 –50 g

*not contained in color orange

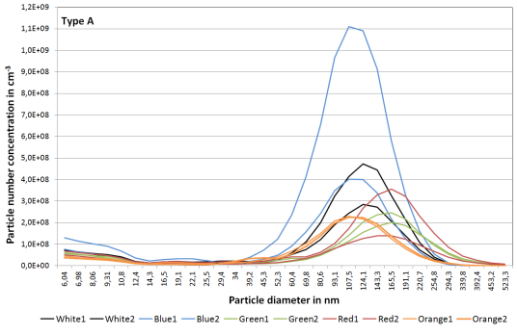

Figure 6. Total particle number concentration vs. particle diameter for Type A smoke generator (various colors)

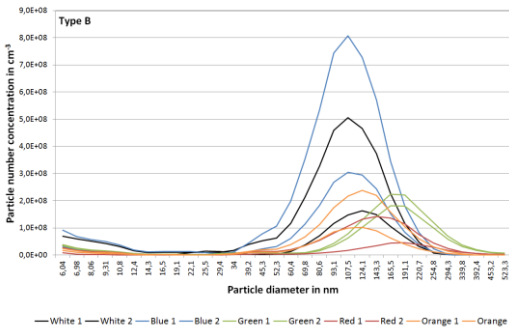

***Figure 7**. Total particle number concentration vs. particle diameter for Type B smoke generator (various colors)*

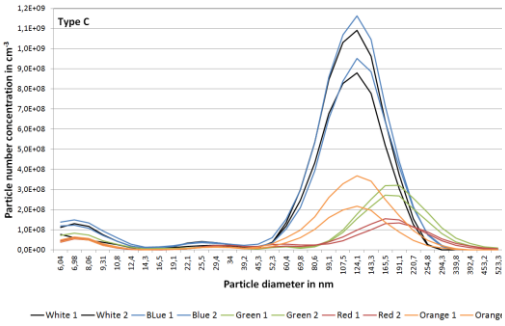

***Figure 8**. Total particle number concentration vs. particle diameter for Type C smoke generator (various colors)*

around *ca.* 130 nm for all types. However, for the colors red and green these dominant particle size ranges (*ca.* 90 nm to *ca.* 350 nm) and the corresponding maxima (*ca.* 160 nm to *ca.* 190 nm) were shifted to bigger particle sizes for all four types. In addition, these two colors were found to be always on the lower end of the particle number concentrations.

Figure 6 to Figure 9 also reveal the slight peaks in particle number concentrations for very small particles (6–12 nm) as mentioned before in the text.

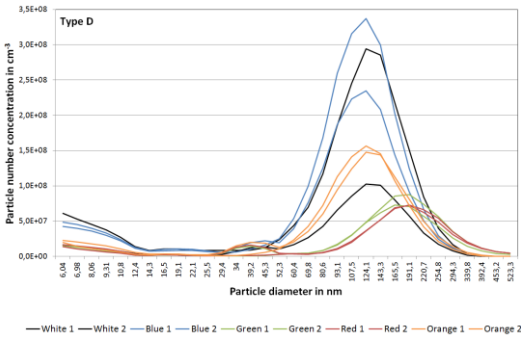

Figure 9. Total particle number concentration vs. particle diameter for Type D smoke generator (various colors)

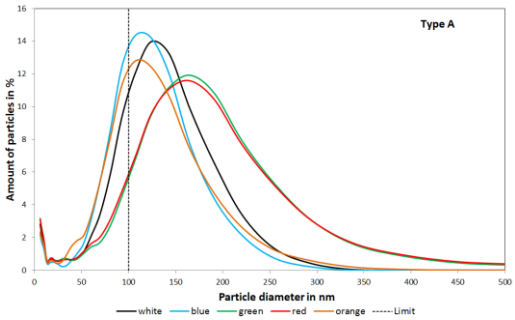

Figure 10. Percentages of particles vs. particle diameter for Type A smoke generator (various colors)

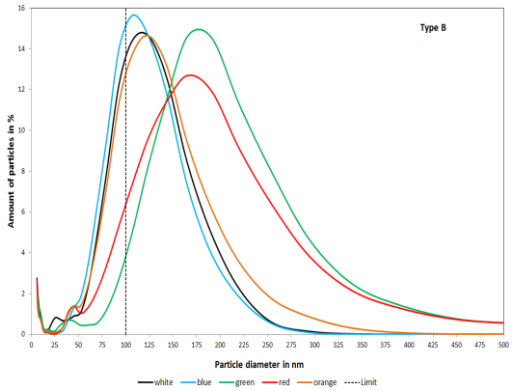

***Figure 11**. Percentages of particles vs. particle diameter for Type B smoke generator (various colors)*

Significant concentrations of particles with diameters greater than 400 nm were not observed for the investigated types and colors.

Considering small particle sizes, which are of specific concern due to the likelihood of entering the alveolar system, a threshold value of 100 nm is displayed in the following figures and evaluated against the particle number distributions of the various smoke generators in Figure 10 to Figure 13. These diagrams show the percentages of the corresponding particle number concentrations based on the total amount of all particles and the particle diameters as a function of the particle diameters. The displayed curves represent the averages of the two measurements of each color.

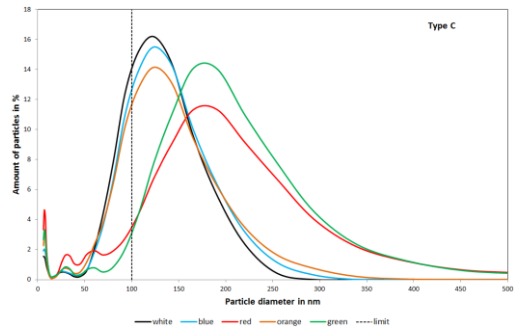

Figure 12. Percentages of particles vs. particle diameter for Type C smoke generator (various colors)

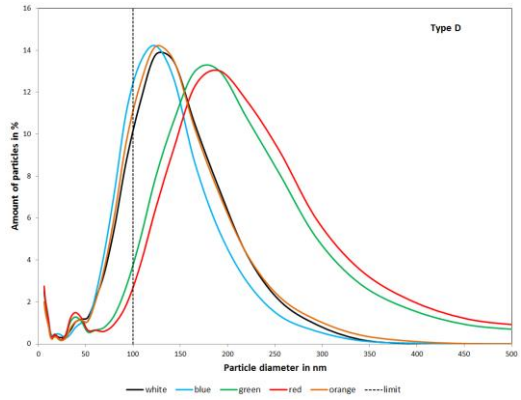

Figure 13. Percentages of particles vs. particle diameter for Type D smoke generator (various colors)

The black dashed lines in the diagrams represent the set threshold and evaluation value of 100 nm.

The above mentioned shift of particle number concentrations to larger particles regarding the red and green colors of all types can be seen clearly in each diagram.

Table 2 displays the minimum and maximum percentage particle number concentration <100 nm and the corresponding colors of each type. As can be seen, the color green emits in all cases the lowest percentage of small particles below 100 nm. It is for all types closely followed by the color red (not displayed in Table 2).

Conclusions

Four different types of smoke generators and five colors per type were investigated regarding their transient behavior of emitting colored smoke. The measurements were performed with a Fast Mobility Particle Sizer (FMPS) offering a particle size range from 5.6 nm to 560 nm.

It was shown that the general transient behaviour of all articles was quite comparable between each other and reproducible to some extent.

However, details regarding the particle size range and the corresponding maxima differed between

Table 2. *Minimum and maximum percentage particle number concentration < 100 nm and the corresponding colors*

Type	Minimum percentage particle number concentration <100 nm, color	Maximum percentage particle number concentration <100 nm, color
Type A	30.3%, green	47.5%, orange
Type B	17%, green	44.4 %, blue
Type C	20.7%, green	38.4%, orange
Type D	20.4%, green	40.7%, blue

the group of colors white, blue, orange and the other two remaining colors green and red. The latter ones showed aerosol emissions in larger particle size ranges when compared to the colors white, blue and orange. Also with regard to the distribution in percentage it was evident that green and red always emitted the least amount of particles below 100 nm. Generally speaking, particles of sizes smaller than 100 nm can easily penetrate the alveolar system of the human lungs and therefore represent a certain hazard. These ultrafine particles are known to adversely affect health and should be minimized, if possible.

Based on the findings of this study, the likelihood of particles entering the alveolar system is slightly reduced for both colors green and red of the four investigated types when compared with the three other colors white, blue and orange. However, there was still a significant number of particles smaller than 100 nm emitted during functioning which has to be considered from all involved parties, like manufacturers, users and test institutes like notified bodies in Europe.

With regards to the intended use, it is still recommended to pay specific attention on this hazard of inhaling aerosols emitted by these products. Corresponding labelling requirements should take this into account by certain mandatory phrases on the label of these products such as:

“Don't inhale the smoke”, “Only for outdoors”, “Suitable protection measures shall be used”

In addition, product specific training measures offered by the manufacturers could be used to increase the awareness of the users regarding these products and the associated hazards.

Further development of smoke generators which focusses on reaction mechanisms, chemical components and the general design of the articles could see the reduction or elimination of particles with diameters <100 nm being produced by these types of devices.

These products, when used correctly and for the intended purposes, remain a low hazard pyrotechnic article and thus are included in category P1; however, the problem of possible exposure to these emitted aerosols during illegal use of such products, e.g. in football stadiums or enclosed areas etc., remains as it is and will likely not change anytime soon. Raising the awareness of the general public regarding the potential hazard of inhaling smoke particles of small sizes is generally reasonable.

References

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2 DIRECTIVE 2007/23/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 May 2007 on the placing on the market of pyrotechnic articles; *Official Journal of the European Union* L 154/1; 14.6.2007.

3 EN 16263 Standard series for pyrotechnic articles - Other pyrotechnic articles, consisting of five parts, CEN/TC 212 WG5, 2015.